



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 013 648 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
28.06.2000 Bulletin 2000/26

(51) Int. Cl.<sup>7</sup>: C07D 305/06

(21) Application number: 99125436.8

(22) Date of filing: 20.12.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 21.12.1998 JP 36286198

(71) Applicant: Toagosei Co., Ltd.  
Minato-ku, Tokyo 105-8419 (JP)

(72) Inventors:  
• Ito, Naokazu  
Minato-ku, Nagoya-shi, Aichi, 455-0027 (JP)  
• Sasaki, Hiroshi  
Minato-ku, Nagoya-shi, Aichi, 455-0027 (JP)  
• Kuriyama, Akira  
Minato-ku, Nagoya-shi, Aichi, 455-0027 (JP)

(74) Representative:  
WILHELM, KILIAN & PARTNER  
Patentanwälte  
Eduard-Schmid-Strasse 2  
81541 München (DE)

### (54) Method for storage stabilization of compounds with oxetane rings

(57) Storage stabilization of compounds with an oxetane ring or oxetane rings, which are useful as ring opening polymerizable monomers, is improved by addition of basic compounds thereto. The basic compound is preferably an alkali metal hydroxide or an amine. The compound with an oxetane compound preferably has a substituent at the 3- or 2-position thereof. Addition amount of the basic compound is preferably 0.1 to 1,000 ppm by weight, more preferably 1 to 1,000 ppm by weight per the compound with an oxetane.

## Description

[0001] The present invention relates to a method for storage stabilization of compounds with oxetane rings (hereunder referred to as "oxetane compounds") that are useful as ring opening polymerizable monomers.

5 [0002] Oxetane compounds are 4-membered cyclic ethers that are known to undergo ring opening polymerization with cationic polymerization catalysts such as Lewis acids. Oxetane compounds are described, for example, in ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, Vol.10, p.653-670. These oxetane compounds are used as raw materials, intermediates and additives for resins, coating agents, adhesives and the like, by taking advantage of their ring opening polymerization properties.

10 [0003] However, when oxetane compounds are stored over long periods, ring opening polymerization occurs as a result of contamination by trace impurities during production, causing a problem in terms of product quality because of clouding due to the resulting polymers.

15 [0004] The method for production of oxetane compounds described by Pattison in the Journal of the American Chemical Society (J. Am. Chem. Soc.), 79, 3455 (1957) is a method of synthesizing oxetane compounds by ester exchange reaction between 1,3-diols and dialkylcarbonates to obtain 6-membered carbonates, and then heating and decarboxylating the product. Research by the present inventors, however, has demonstrated that oxetane compounds produced by this process, such as 3-methyl-3-hydroxymethyloxetane and 3-ethyl-3-hydroxymethyloxetane, often undergo clouding during long-term storage.

20 [0005] It is an object of the present invention to provide a method for storage stabilization of oxetane compounds that prevents clouding of oxetane compounds and avoids their quality deterioration over long periods.

25 [0006] As a result of diligent research aimed at solving the aforementioned problems, the present inventors have completed the present invention upon finding that addition of basic compounds can improve the storage stability of oxetane compounds without impairing their functions including ring opening polymerization.

[0007] In other words, the present invention relates to a method for storage stabilization of oxetane compounds which is characterized by adding basic compounds thereto.

30 [0008] The present invention provides means for solving the problems described above, and is briefly described as claims. The nature, principle and utility of the invention will become more apparent from the following detailed description with reference to the accompanying drawings.

[0009] The invention will now be explained in greater detail.

35 [0010] As oxetane compounds of the invention there may be mentioned 3,3-dialkyloxetanes, 3-alkyl-3-hydroxymethyloxetanes, 3-alkyl-3-chloromethyloxetanes, 3-alkyl-3-alkyloxyoxetanes, 3-alkyl-3-phenyloxyoxetanes, bis(3-alkyloxetan-3-ylmethyl) ethers, 2-alkyloxetanes, 2-phenyloxetanes, 2,2'-dialkyloxetanes, 2,3-dialkyloxetanes and 2-phenyl-3,3-dialkyloxetanes, among which are preferred oxetane compounds with substituents at the 3- or 2-position thereof as they more readily exhibit the effect of the invention, and 3-alkyl-3-hydroxymethyloxetanes are especially preferred.

40 [0011] As the basic compounds for use in the invention there may be used basic inorganic compounds such as alkali metal hydroxides and the like, and basic organic compounds such as amine compounds and the like. As basic inorganic compounds there may be mentioned lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, magnesium hydroxide, calcium hydroxide and potassium carbonate, among which alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide are preferred from the standpoint of solubility in oxetane compounds.

45 [0012] As basic organic compounds there may be mentioned amines as well as nitrogenous heterocyclic compounds such as quinolines and quinolines, among which amine compounds are preferred from the standpoint of compatibility with oxetane compounds; as examples there may be mentioned octylamine, naphthylamine, xylenediamine, dibenzylamine, diphenylamine, dibutylamine, dioctylamine, dimethylaniline, quinacridine, tributylamine, trioctylamine, tetramethylethylenediamine, tetramethyl-1,6-hexamethylenediamine, hexamethylenetetraamine and triethanolamine.

50 [0013] Oxetane compounds are often used in resins and coating agents, taking advantage of their property whereby ring opening polymerization is caused by cationic polymerization catalysts such as Lewis acids, in which case the basic compound functions as an inhibitor on ring opening polymerization. The amount of the basic compound to be added in order to ensure stable storage without impairing the function of the oxetane compound is preferably in a range of 0.1 ppm by weight to 1000 ppm by weight as the amount of added basic compound with respect to the oxetane compound, and more preferably in a range of 1 ppm by weight to 1000 ppm by weight. If the amount added is less than 0.1 ppm by weight it is not possible to achieve adequate storage stability, and even if it exceeds 1000 ppm by weight there is no further improvement in storage stability, while the ring opening polymerization may be inhibited instead, possibly impairing the function of the oxetane compound.

55 [0014] Methods of addition of the basic compound to the oxetane compound are not particularly limited, and it may be accomplished with normal mixing conditions. The basic compound may be used in dilution with water or the like, but it is preferably added directly.

Examples

[0015] The present invention will now be explained in further detail by way of examples and comparative examples.

5 Example 1

[0016] Potassium hydroxide was added as a storage stabilizer at 1 ppm by weight, 10 ppm by weight and 100 ppm by weight to 3-ethyl-3-hydroxymethyloxetane produced by the above-mentioned Pattison method using trimethylolpropane and diethyl carbonate as the raw materials, and each mixture was stored in a thermostatic chamber at 25°C.

10 1) The storage stability was evaluated by the following method, and the results are shown in Table 1.

The mixture was diluted 100-fold with distilled water and the transmittance was measured at a wavelength of 600 nm with a spectrophotometer. The same test was conducted again after 40 days and after 60 days, after which the storage stability was evaluated based on the changes in the values.

15 2) The polymerization was evaluated by the following method, and the results are shown in Table 1.

An alicyclic epoxy UVR-6110 (trade name) by Union Carbide Co. and a photoinitiator UVI-6990 (trade name) by Union Carbide Co. were mixed with the 3-ethyl-3-hydroxymethyloxetane obtained above at a weight ratio of 3-ethyl-3-hydroxymethyloxetane/UVR-6110/UVI-6990 = 20/80/3. The resulting composition was coated onto a steel sheet to a thickness of about 20 microns. Using a conveyer-type ultraviolet irradiation apparatus equipped with an 80 w/cm condensing high-pressure mercury lamp (lamp height = 10 cm, irradiation intensity: 310 mW/cm<sup>2</sup>, 76 mJ/cm<sup>2</sup>), the conveyer speed was changed and measurement was made of the maximum conveyer speed (m/min) at which stickiness was eliminated from the surface thereof. The condition of any stickiness on the cured surface obtained at that time was also evaluated.

A faster conveyer speed indicates earlier curability.

25 Comparative Example 1

[0017] A test was conducted in the same way as Example 1 except that no potassium hydroxide was added; the results are shown in Table 1.

30 Comparative Example 2

[0018] A test was conducted in the same way as Example 1 except that potassium hydroxide was added at 10,000 ppm by weight; the results are shown in Table 1.

35 Example 2

[0019] A test was conducted in the same way as Example 1 except that tri-n-butylamine was added at 10 ppm by weight and 100 ppm by weight; the results are shown in Table 1.

40

45

50

55

Table 1

	Additive	Amount added (ppm)	Storage stability test			Polymerization	
			Change in transmittance with time (%)			Conveyer speed (m/min)	Stickiness on surface
			Day 0	Day 40	Day 60		
Example 1	KOH	1	100	100	99.1	30	no
	"	10	100	100	100	30	no
	"	100	100	100	100	30	no
Example 2	TBuA	10	100	100	100	30	no
	"	100	100	100	100	30	no
Comp. Ex. 1	none	0	100	97.6	92.9	30	no
Comp. Ex. 2	KOH	10,000	100	100	100	10	yes

KOH: potassium hydroxide,

TBUA: tri-n-butylamine

Polymerization: conveyer speed (m/min) and condition of surface stickiness

**Example 3**

[0020] Sodium hydroxide was added as a storage stabilizer at 10 ppm by weight and 100 ppm by weight to 3-methyl-3-hydroxymethyloxetane produced by the Pattison method using trimethylolethane and diethyl carbonate as the raw materials, and each mixture solution was stored in a thermostatic chamber at 25°C. The stability and polymerization were evaluated in the same way as Example 1, and the results are shown in Table 2. However, the changes in transmittance with time were judged after 20 days and 40 days.

**Comparative Example 3**

[0021] A test was conducted in the same way as Example 3 except that no sodium hydroxide was added; the results are shown in Table 2.

**Comparative Example 4**

[0022] A test was conducted in the same way as Example 3 except that sodium hydroxide was added at 10,000 ppm by weight; the results are shown in Table 2.

Table 2

	Additive	Amount added (ppm)	Storage stability test			Polymerization	
			Change in transmittance with time (%)			Conveyer speed (m/min)	Stickiness on surface
			Day 0	Day 20	Day 40		
Example 3	NaOH	10	100	100	100	30	no
	"	100	100	100	100	30	no
Comp. Ex. 3	none	0	100	92.5	87.3	30	no
Comp. Ex. 4	NaOH	10,000	100	100	100	10	yes

NaOH: sodium hydroxide

Polymerization: conveyer speed (m/min) and condition of surface stickiness

[0023] According to the method of the invention, it is possible to improve the storage stability of oxetane compounds without impairing their ring opening polymerization, by addition of basic compounds to the oxetane compounds.

[0024] While there has been described what are at present considered to be preferred embodiments of the invention, it will be understood that various modifications may be made thereto, and it is intended that the appended claims 5 cover all such modifications as fall within the true spirit and scope of the invention.

**Claims**

1. A method for storage stabilization of a compound with an oxetane ring or oxetane rings, which is characterized by 10 adding a basic compound to the compound with the oxetane ring.
2. A method according to claim 1, wherein the basic compound is at least one selected from the group consisting of an alkali metal hydroxide and an amine compound.
- 15 3. A method according to claim 1 or 2, wherein the compound with an oxetane ring has a substituent at the 2- or 3-position thereof.
4. A method according to any one of claims 1 to 3, wherein the compound with an oxetane ring is a 3-alkyl-3-hydroxymethyloxetane.
- 20 5. A method according to any one of claims 1 to 4, wherein the basic compound is added in an amount of 0.1 to 1,000 ppm by weight per the compound with an oxetane.
- 25 6. A method according to claim 5, wherein the basic compound is added in an amount of 1 to 1,000 ppm by weight per the compound with an oxetane.

30

35

40

45

50

55